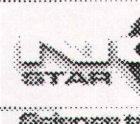




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Final Report: A Novel Approach To Prevention of Acid Rock Drainage (ARD)

EPA Contract Number: 68D00276

Title: A Novel Approach To Prevention of Acid Rock Drainage (ARD)

Investigators: Olson, Gregory J.

Small Business: Little Bear Laboratories Inc.

EPA Contact: Manager, SBIR Program

Phase: II

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RFA: SBIR - Phase II (2000)

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Description:

The goal of this research project was to determine the effectiveness of thiocyanate as an agent to control and/or prevent acid rock drainage (ARD), a serious environmental problem in the United States and around the world. ARD occurs from the oxidation of sulfide minerals exposed to air and water by mining. This oxidation, accelerated by the activities of iron-oxidizing acidophilic microorganisms, produces acidic drainage containing heavy metals. Little Bear Laboratories chose thiocyanate because it is highly and selectively inhibitory toward acidophilic microorganisms at low concentrations; inexpensive, relatively stable in acidic environments, and readily and completely biodegraded in "normal" neutral environments.

The dose and efficiency of thiocyanate for stopping biocatalyzed ARD was evaluated in laboratory-accelerated work with several types of sulfidic mine tailings and waste rock from base and precious metal mining operations. Sulfide was loaded into humidity cells, columns, or trays at a scale of 1 to 50 kg. Thiocyanate was either blended with the rock or applied by trickle irrigation at the start of or during the tests. The efficacy of thiocyanate in reducing ARD was evaluated by comparing leach solutions for ARD components (iron, acidity, sulfate, heavy metals). Results with thiocyanate-treated material were compared to untreated controls. Laboratory investigations of the fate of applied thiocyanate also were performed, as were tests for the potential for acidophilic microorganisms to adapt to thiocyanate.

Four major mining companies participated in this project. Teck Cominco, Ltd.; Phelps Dodge Corporation; Barrick and Homestake Mining Company (which merged with Barrick during the course of this project) played a key role in providing samples of tailings and waste rock for testing. These four companies also provided matching funds in supporting the project. In the "option" project, Barrick and Teck Cominco provided facilities, personnel, and analytical results in support of the project. (13.6 to 100 metric tons) of thiocyanate performance in large columns and test pits at their mine sites.

Practical aspects of commercializing thiocyanate for ARD control were addressed in a series of reports produced by consultant Dr. Terry Mudder. These reports covered: (1) chemistry and commercialization, (2) design and economic evaluation of thiocyanate application process, (3) evaluation of encapsulation of thiocyanate for slow release, (4) thiocyanate and environmental regulations, and (5) the degradation of thiocyanate.

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Summary/Accomplishments:

Thiocyanate significantly reduced ARD from samples of tailings and waste rock in accelerated weathering tests. The reduction depended on the specific ARD parameter measured and the test system. Examples of reduction of sulfate from laboratory and field tests of several types of sulfidic materials are shown in Table 1. The percent ARD reduction of sulfate leaching was less in most tests than the percent ARD reduction based on iron leaching. This was most likely due to precipitation in the rock in columns and humidity cells.

The mechanism of action of thiocyanate in reducing ARD (metal sulfide oxidation) is by inhibiting microbial iron oxidation. Solutions in test systems treated with thiocyanate had lower redox potentials than controls. It is likely that at high thiocyanate, microbial metal sulfide oxidation was almost completely inhibited. Remaining ARD production in these tests probably resulted from abiotic metal sulfide oxidation by oxygen. When thiocyanate concentrations in leachates dropped below 10 mg/L, redox potentials increased and biocatalysis of ARD resumed.

In some cases, thiocyanate was applied only at the beginning of a test at an initial dose of 20 to 200 mg/kg. Results improved by periodic application of deionized water over a period of several months. In other cases, thiocyanate was applied continuously by adding water-soluble KSCN to leach water. Small column adsorption tests indicated test samples bound from 1 to 10 mg SCN/kg.

Copper thiocyanate was shown to be an effective slow- or controlled-release form of thiocyanate. It is not water soluble in acidic, oxidizing solutions characteristic of ARD. In large (approximately 25 kg) humidity cell tests, CuSCN as well as KSCN, but was not as rapidly leached from sulfidic rock. The disadvantage of CuSCN is that copper is relatively toxic to microorganisms. In situations where dissolved copper can be tolerated, CuSCN is promising as a slow-release form of thiocyanate. Additionally, it may be less susceptible to biodegradation at neutral pH than soluble forms of thiocyanate.

Microbial adaptation to thiocyanate was not significant, nor was there evidence for biodegradation of thiocyanate. However, thiocyanate was slowly hydrolyzed at low pH abiotically, producing ammonia. Hydrolysis was faster at higher thiocyanate concentrations. These observations are consistent with published reports of the abiotic autoreduction of Fe^{3+} -thiocyanate complexes.

Field tests at the 13.6 to 100 metric ton scale at mine sites showed thiocyanate (as KSCN) applied at the start at 50 mg/kg could reduce ARD by 50 percent or more from waste rock and sulfidic ore over a test period of 4 to 5 months. These results indicated that microorganisms, as opposed to chemical oxidation by atmospheric oxygen, were responsible for more than 50 percent of the ARD formation.

Table 1. Thiocyanate (KSCN) Performance Against ARD: Reduction of Sulfate and Acidity in Leach Solutions Compared to Untreated Controls from Representative Laboratory and Field Tests.

Type of Material	Test ID	Scale, kg	SCN Applied	Dose, mg/kg	Duration, Months	# Soln Applications	Total Liters Applied ¹	%ARD Red'n (Sulfate)
Carlin ore	BC50-3	24	At start only	199	9	6	6.7	85
Carlin ore	BC50-6	25	At start only ²	194	9	6	6.7	81
Carlin ore	BC-6	1.5	At start only	200	5	4	0.8	91
Carlin ore	BC-11,12	1.5	At start only	49	4	3	0.6	71 ⁴
Carlin ore	BC-3,4	1.0	At start ³	57	5	6	1.15	79
Carlin ore	Field	13600	At start ³	57	5	6	1000	56
Cu tailings	PD 3-6	1.0	At start only	150	5.5	2	0.5	70 ⁵
Cu tailings	Tray 3	37	Biweekly	5-8	6.5	14	32	50
Cu tailings	Tray 4	37	Biweekly	27-40	6.5	14	32	47
Waste rock	RD-3	45	Biweekly	7	6	13	29	34
Waste rock	RD-4	45	Biweekly	33	6	13	29	75

Waste rock	Field	100000	At start only	25	4	rainfall only	unknown	52
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¹ After system initially was brought to saturation.

² CuSCN.

³ Second application of 17 mg SCN/kg was made after 4 months.

⁴ Mean of duplicates.

⁵ Mean of four replicates.

⁶ Free acidity value (total acidity not measured), dissolved iron was reduced by 68 percent.

A series of technical reports by Dr. Mudder identified sources of thiocyanate, regulations on its use, treatment and degradation. The cost for using thiocyanate to prevent acid mine drainage in a hypothetical 25,000 ton per day mine was estimated at 25 cents per ton of ore. This operation was assumed to produce 5,000 tpd of ore, 10,000 tpd of producing waste rock, and 10,000 tpd of acid-producing waste rock. A commercial facility was designed for the application of thiocyanate to waste rock in haul trucks taking rock from the mine pit to waste rock dumps. Capital and operating costs for a thiocyanate application facility were developed.

Conclusions:

Thiocyanate is highly effective in stopping the biocatalyzed component of ARD. As long as thiocyanate is maintained in waste rock or tailings, a substantial fraction of ARD can be eliminated. The extent of ARD reduction by thiocyanate depends on the extent that microorganisms contribute to ARD production in a particular environment or test system—thiocyanate does not inhibit abiotic sulfide oxidation by oxygen. Consequently, thiocyanate should be effective in ARD reduction in environments where microorganisms are active in sulfide oxidation. Where abiotic oxidation of sulfides is more significant, thiocyanate is less effective. Results from field trials at a 13.6 to 100 metric ton scale over 4 to 5 months showed ARD reductions (as measured by sulfate in leach solutions) of 50 percent to more than 75 percent. Thus, at a minimum, microorganisms were responsible for 50-75 percent of the ARD in these environments over the course of the test. However, it is likely that biooxidation was more significant than shown by these figures, because thiocyanate largely was leached out of the test systems after 2 to 3 months. Following thiocyanate application, ARD parameters were reduced 79 percent (sulfate) to more than 90 percent (acid) in the 13.6 tonne test and 74 percent (sulfate) to 79 percent (acidity) in the 100 tonne test. Laboratory scale results were reasonably predictive of larger scale (tons) performance.

Thiocyanate is relatively stable at low pH, being hydrolyzed only slowly to produce ammonia. There was no evidence of adaptation to or metabolism of thiocyanate by acidophilic microorganisms. However, comprehensive control of ARD requires a process to also control abiotic oxidation of sulfides. In this connection, preliminary results using a combination of thiocyanate and iron were encouraging. This approach might be an effective tool for the most efficient reduction of ARD in environmental settings.

Although readily available commercially, thiocyanate also is a component of certain process solutions, especially in metal mines. In these situations, existing solution management and heap closure strategies may merit reexamination. For heap closure, steps could be taken to maintain residual thiocyanate in a heap rather than rinsing.

Publications and Presentations: Total Count: 2

Type	Citation	Journal
Meeting	Olson GJ, Clark TR, Mudder TI, Logsdon M. Control and prevention of microbially catalyzed acid rock drainage with thiocyanate. Submitted to the 2004 Annual Meeting of the Society for Mining, Metallurgy, and Exploration, Denver, CO, March 2004.	nc
Presentation	Olson GJ, Clark TR, Mudder TI, Logsdon M. A novel approach for the prevention of acid rock drainage. To be presented at the Sixth International Conference on Acid Rock Drainage, Cairns, Australia, July 2003.	nc

Supplemental Keywords:

acid rock drainage, ARD, thiocyanate, KSCN, CuSCN, sulfidic mine tailings, mining, waste rock, metal sulfide oxidation

potential, biooxidation, SBIR. , Ecosystem Protection/Environmental Exposure & Risk, RFA, Scientific Discipline, Water, Chemical Engineering, Chemical Mixtures - Environmental Exposure & Risk, Chemistry, Chemistry and M Ecological Effects - Environmental Exposure & Risk, Ecological Effects - Human Health, Ecological Indicators, Ec Protection, Ecosystem/Assessment/Indicators, Engineering, Chemistry, & Physics, Environmental Chemistry, Env Engineering, Fate & Transport, Hazardous, Hazardous Waste, National Recommended Water Quality, Wastewat research environmental biology, ARD, acid mine drainage, acid rock drainage, copper, industrial wastewater, min wastes, municipal wastewater, sulfide

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